

HYDROGASIFICATION OF OIL SHALE IN A CONTINUOUS FLOW REACTOR

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INTRODUCTION

Satisfaction of the projected needs for pipeline gas from a domestic source will ultimately require supplementing the available natural gas with gas produced from the large reserves of solid fossil fuels, coal and oil shale. The time when natural gas will have to be supplemented by the gasification of solid fossil fuels depends on many factors. These factors, along with information on the potential reserves of solid fossil fuels and processes for the production of pipeline gas, have been discussed by Linden (4).

Oil shale is a carbonate mineral which rather tenaciously holds oil-yielding hydrocarbons called kerogen. The production of pipeline gas from this kerogen requires the addition of sufficient hydrogen (hydrogasification) or subtraction of enough carbon (pyrolysis) to convert it into methane or a mixture of methane, ethane and hydrogen having burning properties similar to methane. The most attractive present technique for producing pipeline gas from oil shale is by hydrogasification.

A major processing problem with oil shale arises from the fact that the pipeline gas forming reactions are accompanied by side reactions which occur at significant rates. The major side reactions are mineral carbonates (calcite and dolomite) decomposition, liquid formation, and carbon deposition. Maximum heat economy and kerogen utilization can be obtained if these side reactions are minimized to the greatest extent possible.

The objective of the present work was to develop sufficient information to allow design of a prototype plant for the economic production of pipeline gas from oil shale. Studies were carried out on a pilot plant scale in a continuous-flow tubular reactor. The study evaluated the effects of important process variables such as the hydrogen-to-shale feed ratio, feed gas composition, shale space velocity, pressure, temperature, gas-solid contacting scheme, and oil shale feed stock.

EXPERIMENTAL

Equipment

The hydrogasification unit used in this study consisted of an interconnected feed hopper, a screw feeder, a reactor tube, a discharge star gate, and a residue receiver. A drawing of the assembled unit, showing dimensions and relative positions of the vessels as well as working pressures and temperatures, is given in Figure 1. The flow and instrumentation diagram for the entire plant is shown in Figure 2.

The feed gas was fed into the top of the reactor cocurrently with the shale. The product gas was taken out at the top of the residue receiver, and was passed through porous stainless steel filters, a water-cooled condenser and cartridge filters filled with glasswool, for final cleanup. Pressure was maintained on the hydrogasification unit by an externally loaded back-pressure regulator. Feed gas flow was controlled manually by a needle valve and was metered by a plate orifice.

The shale bed level was controlled by means of a differential pressure measurement by probes set at the desired bed level and at the reactor top. A change in the differential pressure reading of 10 inches of water column (full scale) between the bed and the reactor top corresponded to a change in the bed level of about 4 inches. In moving-bed tests, the shale space velocity was set by setting the bed height and the shale feed rate.

The reactor was heated externally by an electric furnace having eight individually controlled heating zones. Reactor temperatures were measured by eleven Chromel-Alumel thermocouples placed in an interior thermowell. Reactor outside wall temperatures were measured at the center of each heating zone. Reactor pressure, reactor differential pressure, and the hydrogen orifice differential pressure were recorded. Product gas volume was measured with a tin case meter. The specific gravity and heating value of the product gas were measured and recorded continuously.

Procedure

Colorado shale was obtained from the Union Oil Co. mine at Grand Valley, Colorado. The material was selected because of its availability in amounts required for pilot plant testing (approximately 200 pounds per run) and because it is typical of shale from the Green River deposit. New Albany shale was selected as representing a promising Eastern shale. A typical Colorado oil shale ultimate analysis is shown below:

	<u>Wt. % (dry basis)</u>
Ash	59.21
Organic Carbon	18.05
Hydrogen	2.54
Sulfur	0.85
Oxygen (By difference)	13.87
Nitrogen	0.46
Mineral Carbon	<u>5.02</u>
TOTAL	100.00

Feed shale was prepared in batches by crushing the 6-inch chunks to -10 +55 or to -55 +200 U.S.S. sieve size and drying in a steam-heated oven.

Prior to beginning a test, the reactor tube was heated to the desired operating temperature, the feed hopper was filled with shale, and all vessels were purged with nitrogen, depressurized, and then repressurized to the desired operating pressure with feed gas. In moving-bed tests, the reactor tube was initially filled to the desired operating level with inert material prior to starting the run so that steady operating conditions could be obtained more quickly.

When the proper flow of feed gas had been established and was steady, the screw feeder was started. This feeder was calibrated so that the rate of flow of solids could be predicted from the feed rate. Actual feed rates, however, were obtained by measurement of the weight of solids removed from the hopper divided by the elapsed time of the run. Simultaneously with the start of screw feeder, the discharge star feeder was set into rotation. The star was operated either at a rate just sufficient to hold the bed level at the predetermined position or, as in the free-fall tests, at a maximum rate so that no shale bed could be built up within the reactor tube.

With hydrogen feed, as a run progressed, the product gas would gradually increase in gravity and in heating value. Steady values were reached during the latter part of a run. All test results were based on the steady-state portion of the run. Gas samples taken directly from the reactor, however, were found to approach steady values much more quickly than those taken after the product gas passed through the residue receiver, which indicates that steady state conditions were achieved quite rapidly in the bed and that the approach of the product gas to steady state was slow because of back-mixing of the product gas in the residue receiver. In all runs there was an adequately long steady period. In a typical run, using a shale rate of 35 pounds per hour and a 4-foot deep bed, the material in the reactor was completely replaced approximately 20 times.

Liquid rates were measured during the run by means of high pressure Jerguson gages in the bayonet and condenser knockout pots. Liquid recoveries were usually incomplete, due in part to absorption of the liquids on the residue in the receiver hopper.

After completion of a test, the unit was depressurized, purged, and allowed to cool. Feed remaining in the feed hopper, the solid residue in the solids receiver and the liquid products were removed and weighed. Feed and residue solids were given complete chemical analyses and were screened to determine the degree of particle degradation. Residue solids were sampled from near the top of the receiver in order to obtain material representative of steady operation. Liquid products were analyzed for carbon and hydrogen and specific gravity. Product gases were analyzed with a mass spectrometer - except that carbon monoxide was determined by infrared analysis.

The residue rate was calculated from the feed rate and an ash balance between the feed and residue. Feed and product gas rates for the steady-state period were corrected for pressure and temperature and reported in standard cubic feet per hour (at 60° F. and 30.00 inches of mercury), on a dry basis. Gas heating value and specific gravity were computed from gas on a dry gas basis at standard conditions (5).

Process Variables Studied

The range of process variables studied are given below.

Hydrogen-to-shale feed ratio: 0 to 200 percent of the stoichiometric requirements for complete conversion of the organic carbon and hydrogen content of the shale to methane.

Temperature: 1150° to 1360°F.

Total Pressure: 400 to 1600 p.s.i.g.

Shale space velocity: 50 to 900 pounds per cu. foot-hour in moving bed tests (residence time 6 to 90 minutes, and in free-fall tests shale residence times approximately 3 seconds).

Feed gases: Hydrogen, synthesis gas, nitrogen-hydrogen mixtures, and nitrogen.

RESULTS

Hydrogasification with Hydrogen

The most important variable in determining the degree of conversion of the oil shale to gaseous hydrocarbons was shown to be the hydrogen-to-shale feed ratio. For the sake of consistency this parameter was defined as the actual hydrogen feed rate divided by the stoichiometric amount. This ratio is the percent of stoichiometric hydrogen and denoted by S.

Figure 3 shows how this stoichiometric ratio influences the conversion of organic carbon to gaseous hydrocarbons and residue, the remaining carbon being converted to liquid products. The scatter in the fraction of residual carbon formed is due to varying amounts of liquid absorbed by the spent shale and to experimental error. Selected residue samples were extracted with toluene to eliminate variation due to absorbed liquids. This lessens the scatter considerably as indicated by Figure 3.

As the hydrogen-to-shale stoichiometric feed ratio is increased, the conversion of organic carbon to gas increases, until the ratio is approximately 90 percent, at which point approximately 65 percent of the conversion is obtained. Increasing the amount of feed hydrogen beyond 90 percent of stoichiometric only results in dilution of the product gas with hydrogen and no further significant conversion of kerogen.

The decreasing fraction of hydrogen utilization with increasing stoichiometric hydrogen-to-shale feed ratio is also apparent from Figure 4 which shows the composition of the product gas as a function of the hydrogen-to-shale feed ratio.

Since the objective of this work is to develop a process for converting oil shale to high-B.t.u. gas suitable for pipeline transmission it is necessary to remove the carbon oxides and excess hydrogen. The preferred method of accomplishing this is by catalytic reaction of the carbon oxides with hydrogen to form methane. Since the

methanation reaction involves expensive equipment and lowers the overall process efficiency, it is desirable to minimize the amount of carbon oxides and hydrogen consumed in this reaction. Consequently, the use of excess hydrogen is not desirable and only a relatively limited number of experiments were conducted above 90 percent of the stoichiometric ratio.

Pressure

The only variations in gasification yields and product distributions noted with changes in total pressure between 400 and 1600 p.s.i.g. were the result of changes in the gas phase residence time. Even at the lowest pressures and highest gas rates studied with pure hydrogen, gas phase residence times were sufficiently long to convert the heavier aliphatic intermediates. Liquid products collected were mainly aromatic. These aromatics would be difficult to hydrogenate at even the longest gas phase residence times studied.

Temperature

The average bed temperature has a great effect on the paraffin distribution in the product gas as is shown in Figure 5. The methane-to-ethane molar ratio increases very rapidly at temperatures above 1250°F. Propane and butane increase and pentane appears as the temperature is reduced to 1150°F. Both propane and butane vanish as the temperature approaches 1350°F.

These changes in gas composition are due to the decrease in the rates of hydrogenolysis of the heavier gaseous constituents to methane with decreases in temperatures (8). This verifies the mechanism suggested by the earlier laboratory scale work (2) that the hydrogasification reactions proceed via the stepwise destructive hydrogenolysis reactions of oil vapor through successively lower molecular weight aliphatics and finally to ethane and methane.

There are indications that a maximum of organic carbon conversion for a given stoichiometric hydrogen ratio occurs between temperatures of 1200° to 1250°F. A corresponding increase in residual carbon occurs above 1250°F, while increased liquid formation occurs below 1200°F. These results indicate that there is no incentive in operating an oil shale hydrogasification reactor above 1250°F, because of the increased formation of residual carbon. In addition, there is a rapid increase in mineral carbonate decomposition at higher temperature as shown in Figure 6. A portion of the carbon oxides in the product gas has been suggested (6) to result from the decomposition of groups containing organic carbon-oxygen linkages such as carboxyl groups. Carbon oxides from the decomposition of these groups occurs at temperatures as low as 575°F.(1). However, mineral carbonates are the chief source of carbon oxides.

Shale Space Velocity and Free-Fall Tests

Shale residence time had virtually no effect on the conversion of kerogen in the shale to gaseous hydrocarbons and liquid products. Shale residence times were varied from approximately 3 seconds in free-fall operation to 90 minutes in moving-bed operation, with the majority of the tests being made at a shale residence time of approximately 10 minutes. A comparison of the results of a shale residence time of 90 minutes with the results obtained at 10 minutes, at 90 percent of the stoichiometric hydrogen, showed that the organic carbon conversion only increased from 65 to 72 percent. Extrapolation of these results indicates that a nearly tenfold increase in reactor volume would be necessary to achieve this additional 6 percent conversion. Under the conditions, carbonate decomposition was increased from 34 to 70 percent because of the longer residence time. The 6 percent increase in conversion is offset by the greatly increased reactor size necessary to achieve it and by the increased carbonate decomposition with its detrimental effects on process heat economy, hydrogen utilization and product gas cleanup costs.

Carbonate decomposition decreased with increasing shale space velocity from approximately 70 percent at a shale space velocity of 50 pounds per cu. foot-hour to 34 percent at 800. Further increases in shale space velocity in moving-bed operation were not effective in reducing carbonate decomposition because 34 percent of the carbonate is magnesium carbonate which decomposes at a very high rate (3). However, free fall operation reduced the carbonate decomposition to only 8 percent and made possible the direct production of a high-B.t.u. gas. The effect of this decrease is shown by the much higher hydrocarbon composition of the product gas in Figure 4.

The distribution of organic carbon between gaseous hydrocarbons, liquids, and residual carbon products remained unchanged in free-fall as compared to moving-bed operation. The reaction model described below attempts to rationalize this important fact as well as the observed effect of the hydrogen-to-shale stoichiometric ratio.

Reaction Model

It is known from retorting experience that when an oil shale is heated above 500 to 600°F., oil is evolved. Retorting is usually done at moderate temperatures of the order of 1000°F. and fairly complete evolution of the kerogen is attained.

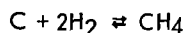
In hydrogasification work conducted by Shultz and Linden (7), conversions of the organic material to gaseous hydrocarbons above 90 percent were obtained. This work was conducted in a batch system which was charged with hydrogen and heated from room temperature to a final temperature of 1300°F. at a heating rate of approximately 9°F. per minute. In marked contrast to this, the heating rate in the present reactor was on the order of 400°F. per second. It is believed that the rapid heating rate in the present work is responsible for the relatively low conversion to gas.

In the present system the shale particles heat so rapidly that a portion of the oil vapor is probably pyrolysed to relatively unreactive aromatics and coke before it can escape from the particle to the gas phase. The rate of evolution of oil vapor is so large that no hydrogen from the gas phase can enter the particle while the vaporization is occurring. This places an upper limit on the conversion to gaseous hydrocarbons, which is represented by the carbon lost to pyrolysis within the shale particle.

The oil vapor which reaches the particle surface without being pyrolysed can either react with hydrogen in the immediate vicinity of the surface of the particle or it can pyrolyze. Thus, one would visualize a gas film surrounding the particle in which both pyrolysis and initial hydrogasification will occur. The extent to which hydrogasification can predominate would seem to be logically a direct function of the rate of mixing of the hydrogen with the oil vapor. It is assumed that the ability of the hydrogen to mix with the oil vapor is a function of the ratio of the hydrogen flow rate to the oil vapor flow rate. This ratio is proportional to the stoichiometric hydrogen to shale feed ratio S . In the lower limit, i.e., zero feed hydrogen, one would not expect zero conversion to gas since gaseous hydrocarbons are a direct product of the pyrolysis reaction.

As these results indicate, at the temperatures employed in these experiments the pyrolysis and hydrogasification reactions are quite rapid. Three seconds is sufficient time to heat the shale particle, evolve and partially pyrolyze the oil. The oil evolved from the surface of the particle travels through the reactor at the gas phase velocity, typically on the order of 0.1 feet per second, which results in a total gas phase residence time of approximately 80 seconds. This residence time of the gas phase is essentially independent of either free-fall or moving-bed operation. Consequently, the gasification results should be, and were, independent of the method of handling the solids.

Following this initial reaction phase, further gasification would necessarily occur by hydrogenation of the residual coke formed by pyrolysis. This coke is apparently quite unreactive to the hydrogen-hydrocarbon gas mixture at the temperatures and residence time employed in these tests. This is due in part to equilibrium hindrance of the reaction



due to the presence of CH_4 .

This conceptual model of the hydrogasification reaction scheme, in addition to explaining the differences between the batch results reported by Shultz and Linden (7) and those reported here, allows an equation to be written which provides a satisfactory fit to the observed results.

The total organic carbon conversion of the shale may be written as,

$$(1) \quad X_{Ri} + X_{Gi} + X_{Ro} + X_{Go} + X_L = 1$$

where

X_{Ri} is the fraction of the kerogen carbon cracked to residue inside the particle.

X_{Gi} is the fraction of the kerogen carbon converted to gas in the particle through the cracking reaction.

X_{Ro} is the fraction of the kerogen carbon cracked to residue outside the particle.

X_{Go} is the fraction of the kerogen converted to gas outside the particle.

X_L is the fraction of kerogen carbon which is converted to liquid products.

The conversion to gaseous hydrocarbons is, therefore,

$$(2) \quad X_{Gi} + X_{Go} = 1 - X_{Ri} - X_{Ro} - X_L$$

On the basis of the model, X_{Ri} is a function of the heatup rate, X_{Ro} a function of both heating rate and the stoichiometric hydrogen feed ratio (a measure of the degree of mixing of the hydrogen with the oil vapor outside the particle) and X_L is also probably a function of heatup rate and the degree of hydrogen mixing. Because of the difficulty of measuring liquid rates in both the pilot plant and laboratory studies it is difficult to determine how X_L was affected by the various parameters. The liquid conversions in the pilot plant varied from 10 to 20 percent. In the batch tests (7) with hydrogen and slow heatup rates very little conversion to liquid products was observed.

A small increase in liquid product formation was noted with increasing hydrogen-to-shale feed ratio in the semiflow (2) tests. This was probably because gas phase residence time decreased in these tests with increasing hydrogen-to-shale feed ratio (hydrogen feed rate). Gas phase residence times were on the order of 10 seconds in these tests which is considerably shorter than the typical 80 second gas phase residence times in the pilot unit. Thus, the most important variable in the formation of liquid products is probably the particle heatup rate assuming sufficient gas phase residence times. This follows from the model since high heatup rates promote pyrolysis which in turn promotes formation of aromatic liquid products which are very difficult to hydrogenate.

Since all of the pilot plant tests were made at essentially the same heatup rates, the following expressions will be written for the various conversion parameters:

$$(3) \quad X_{Ro} = Ae^{-kS}$$

where

A is a function of the heatup rate. This function fulfills the boundary conditions that the $\lim_{S \rightarrow \infty} X_{Ro} = 0$, i.e., perfect mixing, and $X_{Ro} = A$ when $S = 0$, i.e., no hydrogen feed.

$$(4) \quad X_{Ri} = f(q) = B$$

A function only of the heatup rate, essentially constant for the pilot plant tests.

$$(5) \quad X_L = C$$

Assumed a constant for the pilot plant tests.

Substituting from (3), (4) and (5) into (2) gives,

$$(6) \quad X_{Gi} + X_{Go} = 1 - B - C Ae^{-kS}$$

Determination of the constants gives the final equation,

$$(7) \quad X_{Gi} + X_{Go} = X_{Gt} = 0.68 - 0.30 e^{-1.72S}$$

Equation (6) compared with the experimental data in Figure 3 and a reasonable fit is shown. Within the limits of the work done to date the model seems reasonable. It is hoped that future tests will further prove or modify the assumptions and allow a complete description of the process to be given.

Hydrogasification with Synthesis gas and Nitrogen-Hydrogen Mixtures

Operating the process with synthesis gas produced by partial oxidation of shale oil can provide a means of heating the oil shale to reaction temperature at sufficiently low hydrogen to shale ratios that hydrogen separation in the product gas will not be required. The presence of carbon dioxide in the synthesis gas also inhibits the decomposition of calcite (CaCO_3) thus improving hydrogen utilization and process heat efficiency. In an actual synthesis gas run, carbonate decomposition was reduced from 30-40 percent to approximately 20 percent.

Feed gas compositions for synthesis gas evaluation were chosen to be as close as possible to the reported values (10). Since synthesis gas was not available a gas was prepared whose composition at room temperature was the same as synthesis gas would be if cooled down to room temperature assuming water gas shift equilibrium were satisfied. The room temperature composition of this gas was:

<u>Constituent</u>	<u>Mole, %</u>
CO	36.0
CO ₂	15.1
H ₂	48.1
CH ₄	0.6
C ₂ H ₆	0.1
C ₃ H ₈	<u>0.1</u>
TOTAL	100.0

In experimental runs the presence of gaseous constituents in the synthesis gas other than hydrogen did not have an effect on the hydrogasification results within the limits studied. The organic carbon conversion to gaseous hydrocarbons remained to be influenced by the hydrogen-to-shale ratio fed as shown by the general correlation for the conversion of organic carbon to gaseous hydrocarbons in Figure 3.

Alternate processing schemes include the use of steam, hydrogen-steam; or carbon dioxide-steam mixtures (flue gas) in a fluidized-bed reactor. External heat requirements, if necessary, would be furnished by heating coils. Since the process is to be operated at approximately 1200°F., steam and carbon dioxide are assumed to be essentially inert to the gaseous hydrocarbons. This was verified in the synthesis gas tests. Therefore, it was expedient to study the effect of diluents on hydrogasification by making tests with various nitrogen-hydrogen feed mixtures since nitrogen is certain to be inert. The intent was to determine if either the mole fraction hydrogen or the hydrogen partial pressure were important in effecting conversions to gaseous hydrocarbons. These tests employed nitrogen mole fractions from 100 percent to 0 percent. This series of tests correlate nicely with the results achieved with pure hydrogen as shown by Figure 3 indicating that the only important variable was the stoichiometric hydrogen ratio, and that neither the mole fraction or the partial pressure were important parameters.

Hydrogasification of New Albany Shale

New Albany shale was selected as being one of the more promising Eastern oil shales for the manufacture of pipeline gas. A complete survey of the important Eastern shale deposits has been reported by Shultz (9).

New Albany shale has a greater tendency to form carbonaceous residue than does Colorado shale. This is indicated by the table below where representative results with the New Albany shale are reported.

Run No.	57	59	68
Shale Particle Size, U.S.S.	-10 +55	-10 +55	-10 +55
Shale Space Velocity, lb./cu.ft.hr.	688	698	352
Average Bed Temperature, °F.	1219	1273	1261
Hydrogen-to-Shale Feed Ratio, % of Stoichiometric	43	42	205
Organic Carbon Conversion, Gaseous Hydrocarbons	36.3	40.6	53.2
Liquids	6.4	3.0	7.2
Residue	<u>54.0</u>	<u>52.7</u>	<u>34.5</u>
TOTAL	96.7	96.3	94.9

Also, with New Albany shale, the conversion to gaseous hydrocarbons is less dependent on the hydrogen-to-shale feed ratio than with Colorado shale. However, no difference was noted in the gasification behavior of these two materials in batch tests. The same model as presented for the Colorado shale, therefore, may also be valid for the New Albany shale, but insufficient data is available for the New Albany shale to determine the validity of this.

Qualitatively it appears that the Fisher assay oil yield is an important parameter in determining the reactivity of a shale to form gaseous hydrocarbons. For example, the Fisher assay oil yield for the New Albany shale was approximately 0.052 gallons per pound of organic material whereas the Colorado shale oil yield was approximately 0.088 gallons per pound of organic material. The carbon-hydrogen ratios were approximately 7.85 and 7.20 respectively. The lower oil yield with the New Albany material indicates an increased tendency to form residual carbon rather than oil vapor. This tendency of the kerogen to form carbonaceous residue appeared to have a similar effect on the hydrogasification yields.

SUMMARY AND CONCLUSIONS

The production of pipeline gas from oil shale is possible over a wide range of operating conditions. The conversion of the organic carbon in the shale was a function mainly of the hydrogen-to-shale feed ratio being independent of pressure and diluents in the feed gas. A slight effect of temperature was noted at the extremes of the temperature range studied, 1360° to 1150°F. The conversion of kerogen to gaseous hydrocarbons was reduced at the higher temperature level by increased residual carbon formation and at the lower temperature by increased liquid formation. Particle residence

time did not have an effect on product gas properties or conversion of organic carbon to gaseous hydrocarbons. A semi-empirical equation was developed, based on the rate of particle heatup and hydrogen-oil vapor mixing, which allowed the conversion of organic carbon to gaseous hydrocarbons to be predicted. The model indicates that the ideal hydrogasifier design should provide for slow solids heatup rates and rapid hydrogen-oil vapor mixing.

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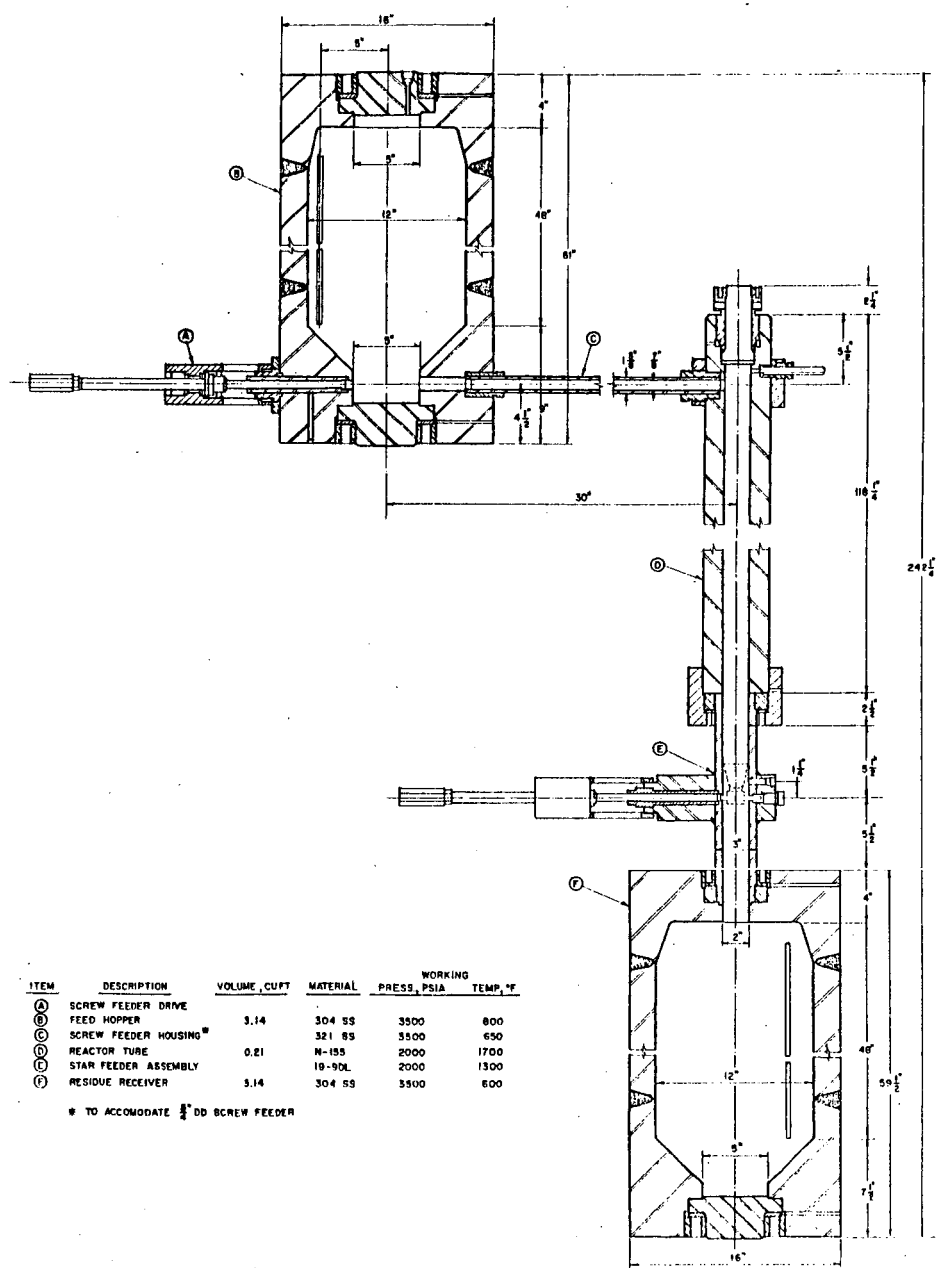


Fig. 1.-OIL SHALE HYDROGASIFICATION PILOT UNIT

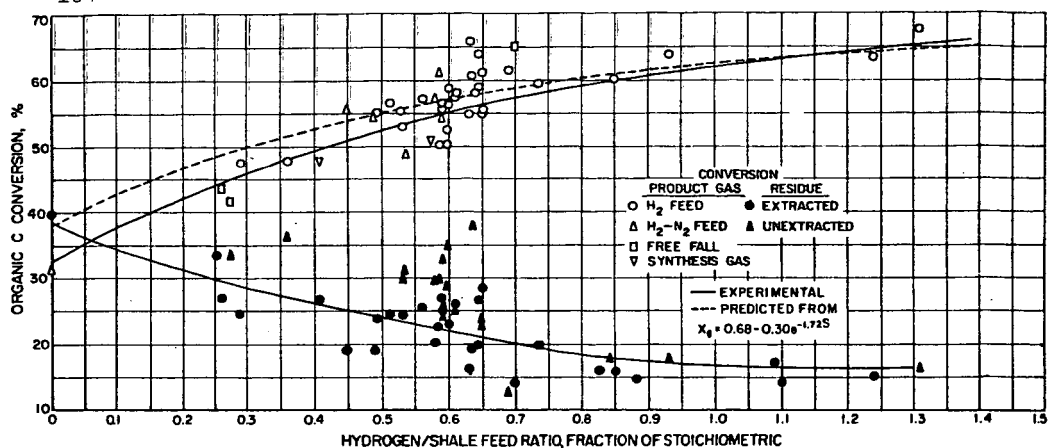


Fig. 3. - EFFECT OF HYDROGEN/SHALE FEED RATIO ON CONVERSION OF ORGANIC CARBON TO RESIDUE AND GASEOUS HYDROCARBONS

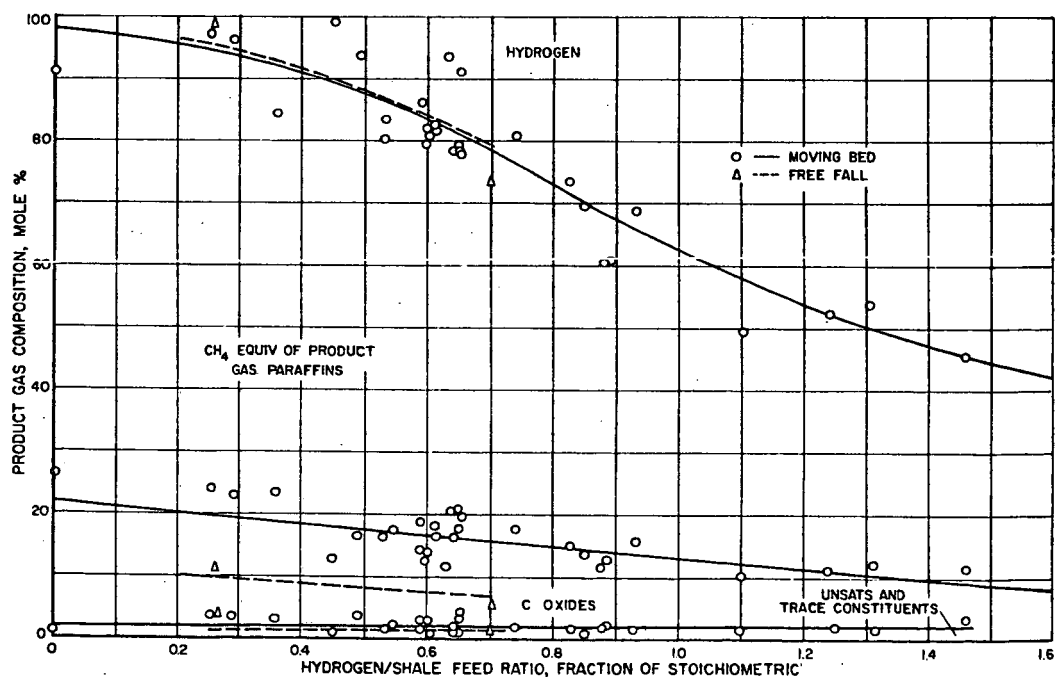


Fig. 4. - EFFECT OF HYDROGEN/SHALE FEED RATIO ON PRODUCT GAS COMPOSITION

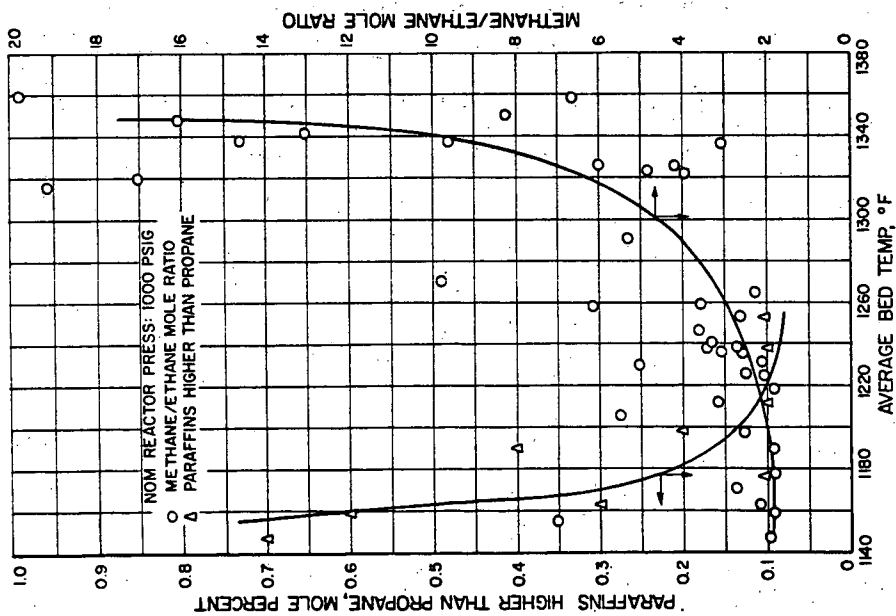


Fig. 5.-EFFECT OF AVERAGE BED TEMPERATURE ON GASEOUS HYDROCARBON DISTRIBUTION

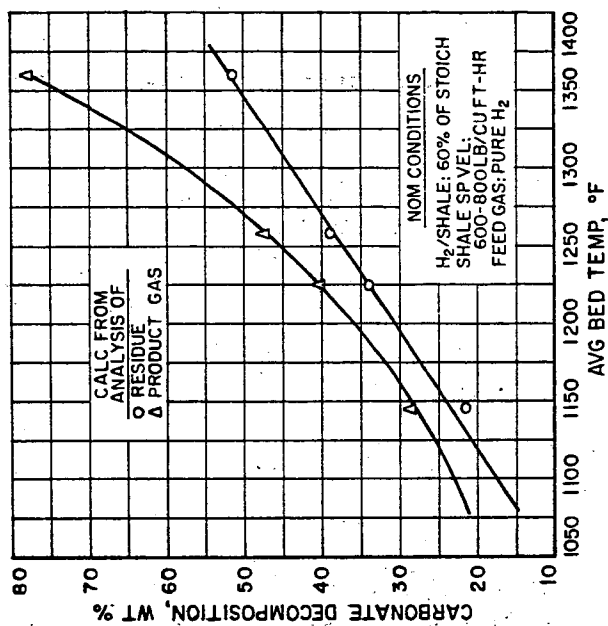


Fig. 6.-THE EFFECT OF AVERAGE BED TEMPERATURE ON CARBONATE DECOMPOSITION